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Adjuvant Effects on the Therapeutic Control of Potato Late Blight by Dimethomorph Wettable Powder Formulations

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Abstract: Dimethomorph is an effective Oomycete fungicide useful for the control of late blight (*Phytophthora infestans*, deB) on potatoes (*Solanum tuberosum*, L.) by preventative (prophylactic) sprays. The results of glasshouse trials using *S. tuberosum* plants inoculated one day prior to treatment showed that the weak to moderate curative (therapeutic) action of a wettable powder formulation of dimethomorph (WP1) could be substantially enhanced by spray tank adjuvants. A limited survey of surfactant adjuvants indicated that enhancements of performance of WP1 varied with the ethylene oxide content in two series of surfactants, C_{12}/C_{14} alcohol ethoxylates ('Genapol' C series) and nonylphenol ethoxylates ('Arkopal' N series). Optimum enhancements were obtained with intermediate degrees of ethoxylation and 'Genapol' C080 was adjudged to be marginally superior to its analogues and superior to all of the 'Arkopal' series, as well as to a silicone ethoxylate/propoxylate ('Silwet' L-77), an alkylamine ethoxylate/propoxylate ('Armoblen' 557), and sodium sulfosuccinate ('Aerosol' OTB). It was also superior to an emulsifiable paraffinic/naphthenic oil (HVI 60E).

Further trials established that relatively high application rates (1000–1500 g ha^{-1}) of 'Genapol' C080 were required for maximum enhancement and that the presence of mancozeb, as a co-fungicide, did not substantially affect the enhancement of the therapeutic performance of dimethomorph by 'Genapol' C080.

Key words: fungicide, dimethomorph, potato, *Solanum tuberosum*, late blight, *Phytophthora infestans*, adjuvants, formulation.

1 INTRODUCTION

Dimethomorph [(*E,Z*)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)acryloyl]morpholine; Log K_{ow} = 2.7] is an Oomycete fungicide with specific activity against members of the family *Peronosporaceae* and the genus *Phytophthora*.[1] In particular it is effective against downy mildew (*Plasmopara viticola* Berl & deB) on vines (*Vitis vinifera* L.) and gives excellent protection against late blight (*Phytophthora infestans*, deB) on potatoes (*Solanum tuberosum*, L).[1] Although it has some curative (therapeutic) action, its main use with the current commercial formulations is as a protectant (prophylactic) fungicide against *P. viticola* and *P. infestans*.

It was reported recently that the therapeutic activity of emulsifiable concentrate (EC) and wettable powder (WP) formulations of dimethomorph against *P. viticola* could be greatly enhanced in glasshouse trials by the use of spray tank adjuvants, in particular alcohol ethoxylates with intermediate ethoxylation (6–10 moles ethylene oxide).[2,3] These findings prompted the question of whether such enhancements of performance could also be achieved against *P. infestans* on *S. tuberosum*. There were indications from preliminary screening tests that some surfactants and emulsifiable oils improved the performance of WP formulations of dimethomorph and that some liquid formulations of dimethomorph containing high amounts of surfactants appeared to be very effective against *P. infestans* on

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both *S. tuberosum* and tomato (*Lycopersicum esculentum* Mill) (C. L. Dunn, J. K. McKinlay-Clarke, pers. comm.).

A limited survey of some types of surfactants and an emulsifiable paraffinic/naphthenic oil for the enhancement of the therapeutic performance of a standard WP formulation of dimethomorph against one-day-old infections of *P. infestans* on *S. tuberosum* plants was therefore undertaken. The study was concluded with an investigation to determine the optimum application rate of the most effective adjuvant and to compare its performance with that of the current commercial formulation of dimethomorph, 'Acrobat MZ'*, containing a second fungicide, mancozeb.

2 EXPERIMENTAL

2.1 Materials

Wettable powder formulations of dimethomorph, with the following compositions: WP1—dimethomorph, 500 g; wetting and dispersing agents, 100 g; kaolin, 400 g; WP2—dimethomorph, 75 g; mancozeb, 600 g; wetting and dispersing agents, 70 g; kaolin to 1 kg, were prepared by air-milling and supplied by the Formulation Chemistry Department at Sittingbourne Research Centre. Adjuvants were obtained from suppliers as follows: C_{12}/C_{14} alcohol ethoxylates, 'Genapol' C050, C080, C100, C200 with 5, 8, 10, 20 moles of ethylene oxide respectively and nonylphenol ethoxylates, 'Arkopal' N060, N100, N150, N230 with 6, 10, 15, 23 moles of ethylene oxide respectively, Hoechst AG, Frankfurt, Germany; silicone ethoxylate/propoxylate, 'Silwet' L-77, Union Carbide Corporation, Connecticut, USA; sodium sulfosuccinate, 'Aerosol' OTB, Cyanamid Ltd, Gosport, UK; alkylamine ethoxylate/propoxylate, 'Armoblen' 557, Akzo Chemical Company, Deventer, The Netherlands; paraffinic oil containing naphthenic components, HVI 60, Shell Chemicals UK, Ely. This oil was mixed with 'Emulsogen' M (Hoechst Chemicals AG) in a ratio of 9 + 1 by weight to render it emulsifiable and designated by the letter E.

2.2 Plants and inoculation procedure

Potato plants (*S. tuberosum* cv. Desiree) were propagated from tuber cuttings in a sterilised loam compost, amended with peat, and grown to the five- to six-leaf stage under growth room conditions (temperature, 10°C; lighting, 12 h photoperiod under lamps of 125 W cool white fluorescent tubes giving 155 μmol m^{-2} s^{-1} PAR). The apices and any side shoots of the plants were removed to leave plants with three well-developed leaves. These leaves were inoculated by spraying the adaxial surface with a suspension of *P. infestans* (3.5×10^4 sporangia ml^{-1}), obtained from either tomato or potato hosts. The inoculated plants were transferred to a dark, high humidity chamber (17°C) for 17–20 h before being removed and the leaves allowed to dry (1–2 h) before spraying.

2.3 Preparation and application of spray solutions

The general procedure was to prepare dispersions of formulations and adjuvants at twice the concentrations required for application and then to mix equal volumes of these formulation and adjuvant dispersions, or water in the case of either no adjuvant or no formulation, immediately before application. For example, for the applications recorded in Tables 1 and 2, amounts of WP1 (0.8, 0.4, 0.2, 0.1, 0.05 g) were dispersed into tap

TABLE 1
Adjuvant Effects on the Efficacy of WP1 in the Therapeutic Control of One-Day-Old Infections of *Phytophthora infestans* on *Solanum tuberosum*

	Effect (%)[b,c] *Dimethomorph application rate (g ha^{-1})*				
Adjuvant[a]	*12·5*	*25*	*50*	*100*	*200*
None	0	7	2	1	26
'Genapol' C050	80	89	**97**	91	96
'Genapol' C080	87	**96**	**96**	**99**	**100**
'Genapol' C100	84	90	**99**	95	90
'Genapol' C200	69	74	83	91	92
'Silwet' L77	37	78	77	83	70

[a] Adjuvant application rate = 1000 g ha^{-1}.
[b] Mean infected leaf area with water-sprayed plants = 50%.
[c] Numbers in **bold** indicate >90% effect at a 95% confidence level.

TABLE 2
Adjuvant Effects on the Efficacy of WP1 in the Therapeutic Control of One-Day-Old Infections of *Phytophthora infestans* on *Solanum tuberosum*

	Effect (%)[b] *Dimethomorph application rate (g ha^{-1})*				
Adjuvant[a]	*12·5*	*25*	*50*	*100*	*200*
None	24	19	21	31	0
'Arkopal' N060	57	74	64	55	57
'Arkopal' N100	0	33	52	90	31
'Arkopal' N150	29	38	62	57	86
'Arkopal' N230	0	38	48	50	14
'Armoblen' 557	29	29	7	10	62
'Aerosol' OTB	0	0	0	0	2

[a] Adjuvant application rate = 10000 g ha^{-1}.
[b] Mean infected leaf area with water-sprayed plants = 42%.

* Acrobat MZ is a registered trademark, former to Shell International Chemical Company and now Cyanamid.

water (250 ml). An amount (1.6 g) of each adjuvant was dissolved in tap water (200 ml) and 20-ml aliquots of these dispersions mixed with 20-ml aliquots of the formulation dispersion. In the three trials examining the effect of varying adjuvant application rate, appropriate amounts of adjuvant were selected so that on final mixing of equal volumes of WP1 (or WP2) and adjuvant dispersions (or water) the concentrations of both components were at the correct levels for the application rates quoted in Tables 3–5. All preparations were applied at a volume rate of 250 litre ha^{-1} to four replicate plants (providing 12 replicate leaves) using a track sprayer equipped with a flat fan hydraulic nozzle (80015, Spraying Systems Co., Illinois, USA) operating at 276 kPa. In all trials four replicate plants were also sprayed with water to act as untreated controls.

2.4 Plant treatment, assessment and statistical analysis

The spray deposits were allowed to dry and the plants returned to a growth room [temperature, 17°C; lighting 16 h photoperiod under sodium lamps (250 W Sont GEC Solarcolor) giving 155 μmol m^{-2} s^{-1} PAR; relative humidity ~70%] and placed in a randomised array on sub-irrigation matting for three days. They were then transferred to a high humidity/low light intensity room (relative humidity 95–100%, light intensity ~50 μmol m^{-2} s^{-1} PAR, temperature (23°C) for 24 h, incorporating a dark period of 8 h. Each inoculated leaf was assayed for infection by visual assessment of the percentage leaf area infected.

The mean value of percentage infected leaf area for the 12 replicates/treatment was converted into percentage effect, as given in the tables, by the expression

$$\text{percentage effect} = [(C - T)/C]100$$

where C and T are the mean values of percentage infected leaf area of water-sprayed control and treated plants respectively.

It was observed from all the trials in this work that for those plants sprayed only with water, or with those treatments that gave little or no control, the extent of variation of infection between replicates, including leaves on the same plant, was high (coefficients of variation up to 100%). There was also variation in overall infectability between trials. This was because of innate variation in the infectability of the potato leaves. It is a well-known phenomenon in this type of work and has no simple cure (C. L. Dunn—pers. comm.). The consequence is that this variation limited the ability to detect significant differences between treatments. Furthermore, the nature of the results, including apparent negative dose–response trends at moderate levels of control, prevented construction of dose–response curves that could be analysed by regression. Comparison of different treatments could, therefore, only be made within trials by conducting a two-way analysis of variance on the original data to assess if there were significant differences in performance between the adjuvants followed by a studentised range test to give a statistical ranking of the adjuvants and t-tests to identify those treatments that gave >90% effect at a 95% confidence level.

3 RESULTS AND DISCUSSION

None of the adjuvant solutions alone, at any application rate, was observed to have any therapeutic control of one-day-old infections of *P. infestans* on *S. tuberosum*. These zero effects have been omitted from the results given in Tables 1–5. Applications of WP1 gave only either low (Tables 1–3, 5) or moderate (Table 4) control with no obvious dose–response trends. These results were in accord with previous observations that the best control of this disease with this formulation of dimethomorph is with applications made before the arrival of the disease, that is, with a preventative (prophylactic) spray schedule.[4]

TABLE 3
Effects of Adjuvant Type and Application Rate on the Efficacy of WP1 in the Therapeutic Control of One-Day-Old Infections of *Phytophthora infestans* on *Solanum tuberosum*

Adjuvant		*Effect (%)*[ab] *Dimethomorph application rate (g ha^{-1})*			
Type	*Application rate (g ha^{-1})*	*25*	*50*	*100*	*200*
None	—	22	31	8	3
HVI 60E	750	32	68	75	93
	1500	86	89	92	93
'Genapol' C080	750	85	86	91	93
	1500	85	**97**	94	**99**
'Arkopal' N150	750	56	58	59	74
	1500	49	81	88	91

[a] Mean infected leaf area with water-sprayed plants = 60%.
[b] Numbers in **bold** indicate >90% effect at a 95% confidence level.

TABLE 4
Effect of 'Genapol' C080 Application Rate on the Efficacy of WP1 in the Therapeutic Control of One-Day-Old Infections of *Phytophthora infestans* on *Solanum tuberosum*

'Genapol' C080 application rate ($g\ ha^{-1}$)	*Effect (%)*[ab] *Dimethomorph application rate* ($g\ ha^{-1}$)				
	12.5	*25*	*50*	*100*	*200*
0	64	51	43	49	64
94	40	19	25	58	35
187	67	29	18	61	49
375	50	36	66	53	8
750	78	88	87	93	89
1500	70	94	93	96	**97**

[a] Mean infected leaf area with water-sprayed plants = 42%.
[b] Numbers in **bold** indicate >90% effect at a 95% confidence level.

However, inclusion of the 'Genapol' alcohol ethoxylates into the dispersions of WP1 increased the level of therapeutic control dramatically, with high levels of control even at dimethomorph application rates of 12.5 g ha^{-1} (Table 1). All of the 'Genapol' surfactants brought about this change in performance of WP1, though C200 was marginally (i.e. not statistically significant at $P = 0.05$) weaker and C080 marginally stronger than the other members of the series.

The silicone ethoxylate/propoxylate, 'Silwet' L-77, also brought about a considerable enhancement of the therapeutic performance of WP1, but the levels were significantly lower (at $P = 0.05$) than those induced by the 'Genapol' series of alcohol ethoxylates (Table 1). This observation was surprising in that it might have been expected that the very low surface tension of the spray solutions containing 'Silwet' L-77 would have promoted entry into the adaxial stomata of *S. tuberosum*,[5] and thus facilitated foliar penetration of dimethomorph to a greater degree than could be achieved by the alcohol ethoxylates which do not reduce spray solution surface tensions sufficiently for stomatal entry. It would seem that foliar penetration of dimethomorph by non-stomatal routes was of greater importance under the conditions of this trial.

A range of nonylphenol ethoxylates ('Arkopal' series) also brought about significant enhancements of the therapeutic activity of WP1 (Table 2). Structure/activity trends were difficult to deduce, though the highest ethoxylate member, with 23 moles of ethylene oxide ('Arkopal' N230), appeared to give the weakest enhancement. This effect also occurred with the 'Genapol' alcohol ethoxylate series suggesting that surfactants with lower degrees of ethoxylation were more efficient activators of foliar uptake of dimethomorph, as observed on vines,[2,3] and in agreement with data on other compounds and surfactants published recently.[6]

Enhancement of performance of WP1 by the alkylamine ethoxylate/propoxylate ('Armoblen' 557) was similar to that by 'Arkopal' N230, while that by sodium sulfosuccinate ('Aerosol' OTB) was non-existent (Table 2). These three surfactants were, therefore, of no further interest for trials with WP1. In the final trial of this brief experimental survey of types of adjuvants for enhancing the therapeutic performance of WP1, the action of the most effective surfactant adjuvant, 'Genapol' C080, was compared with that of an emulsifiable paraffinic/naphthenic oil, HVI 60E (Table 3). Although HVI 60E gave substantial enhancements to the performance of WP1 at both application rates, this was not as good as that obtained with 'Genapol' C080, particularly at the lower application rate of 750 g ha^{-1}. Also included in

TABLE 5
Effect of 'Genapol' C080 Application Rate on the Efficacy of WP1 and WP2 in the Therapeutic Control of One- and Two-Day-Old Infections of *Phytophthora infestans* on *Solanum tuberosum*

Formulation	*'Genapol' C080 application rate* ($g\ ha^{-1}$)	*Effect (%)*[a] *Dimethomorph application rate* ($g\ ha^{-1}$)							
		One-day-old infection				*Two-day-old infection*			
		25	*50*	*100*	*200*	*25*	*50*	*100*	*200*
WP1	0	1	13	39	41	59	4	13	17
	750	—	—	85	**95**	—	—	82	82
	1500	**98**	**97**	**99**	**99**	69	76	84	93
WP2	0	28	20	66	19	0	47	81	23
	750	—	—	75	76	—		57	81
	1500	91	**97**	**97**	**96**	80	92	69	65

[a] Mean infected leaf area with water-sprayed plants = 90% (1 day); 85% (2 days).
[b] Numbers in **bold** indicate >90% effect at a 95% confidence level.

this trial was the best alkylphenol ethoxylate ('Arkopal' N150) which also proved less effective than 'Genapol' C080 (Table 3).

'Genapol' C080 was therefore selected for further investigation, studying the influence of its application rate on the effectiveness of WP1. Addition of C080 up to an application rate of 750 g ha^{-1} made little difference to the moderate performance of WP1 alone. However, higher application rates of 750 and 1500 g ha^{-1} gave considerable enhancements to the performance of WP1, confirming the results from the previous trials (Tables 1, 3). It was therefore clear that, to achieve sufficient therapeutic control of infections of *P. infestans* on *S. tuberosum*, high application rates (1000–1500 g ha^{-1}) of 'Genapol' C080 were required.

In commercial practice, for reasons of combating the onset of resistence of *P. infestans* to dimethomorph, it will always be used in conjunction with a second fungicide. The first commercial formulation, 'Acrobat' MZ, contains a mixture of dimethomorph with mancozeb. It was therefore important to determine whether mancozeb would affect the enhancement of the therapeutic effect achieved by 'Genapol' C080. The enhancement of performance of WP1 and a mancozeb/dimethomorph formulation, WP2, by 'Genapol' C080 at 750 and 1500 g ha^{-1}, showed that the presence of mancozeb did not have any substantial effect on the enhancement action of 'Genapol' C080 (Table 5). Thus an alcohol ethoxylate adjuvant, such as 'Genapol' C080, added to spray tank dispersions of one of the commercial formulations intended for use in control of *P. infestans* on *S. tuberosum* broadened the use of the product from being mainly a prophylactic fungicide into one which also possessed considerable therapeutic fungicidal activity.

Such improvements of performance were probably the consequence of enhanced foliar penetration of dimethomorph induced by 'Genapol' C080 and, if that occurred with plants under field conditions, it could confer advantages such as reduced application rates, improved rainfastness (owing to foliar penetration of dimethomorph) and a wider window for application (owing to control of early stages of infestion within cellular tissue present before application). Field trials to assess the extent of these possible advantages are in progress.

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